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REVIEW ARTICLE

Computational design of heterogeneous catalysts and gas separation materials for advanced chemical processing

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Abstract Functional materials are widely used in chemical industry in order to reduce the process cost while simultaneously increase the product quality. Considering their significant effects, systematic methods for the optimal selection and design of materials are essential. The conventional synthesis-and-test method for materials development is inefficient and costly. Additionally, the performance of the resulting materials is usually limited by the designer's expertise. During the past few decades, computational methods have been significantly developed and they now become a very important tool for the optimal design of functional materials for various chemical processes. This article selectively focuses on two important process functional materials, namely heterogeneous catalyst and gas separation agent. Theoretical methods and representative works for computational screening and design of these materials are reviewed.

Keywords heterogeneous catalyst, gas separation, solvent, porous adsorbent, material screening and design

1 Introduction

A chemical process can be typically decomposed into multiple scales (or levels) where different physical and/or chemical phenomena take place. As illustrated in Fig. 1, molecules or materials are first aggregated into a single or multiphase fluid mixture possessing certain macroscopic properties. Transitioning from chemistry into engineering, the analysis and design of process units are performed. The process units are finally integrated into a chemical plant under the consideration of economics, health, safety, and environmental regulations. The lowest level considers all decisions that are linked to the structures of functional molecules or materials used in a chemical process, for example, catalysts, solvents, and adsorbents. Considering the significant impacts of these functional materials, they must be carefully selected in order to reduce the process cost while simultaneously increasing the product quality. On the other hand, one should note that there are always strong interactions between the selection of materials and the operation of processes. It is due to this reason that all levels involved in a process system should be considered simultaneously, which makes the integrated materials and process design very essential.

The traditional material exploration approach first hypothesizes a material, experimentally synthesize and evaluate it. If the material does not meet the desired properties or performance criteria, then modify the structure and re-perform the experiments. This generate-and-test method is very time-consuming and costly. Moreover, the performance of the finally identified material is limited by the designer's expertise and knowledge. With the exponential growth of computer power as well as the constantly improving theoretical and modeling approaches, it is now possible to apply computational methods to design materials for specific applications. Considering that catalysts and separation agents are two

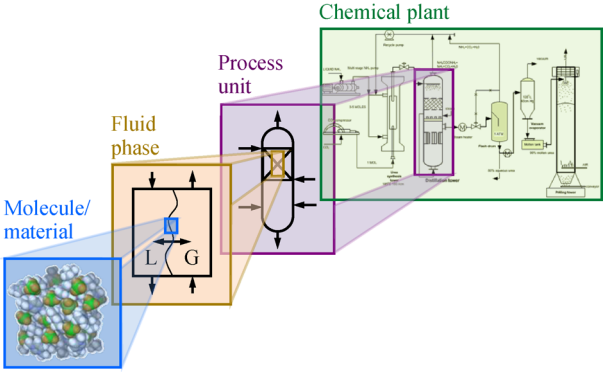

Fig. 1 Multiscale vision of a chemical process.

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most frequently used process materials and distillation is normally used for liquid separation, this article selectively focuses on catalytic and gas separation materials. Methods, research status, and representative work in the computational screening and design of these materials are reviewed.

2 Catalyst design for reactions

Although a chemical reaction may be possible from a thermodynamic point of view, the reaction rate has to be enhanced by a suitable catalyst that allows product formation at relatively mild conditions. Catalysts are used in almost every chemical processes, such as ammonia synthesis, methanol synthesis, hydrocarbon reforming, etc [1]. Most catalysts used in large-scale industrial processes are solids (or heterogeneous) where the gas or liquid reaction takes place on the surface of the catalyst. Traditionally, the search of new catalysts and improvement of existing catalysts have been empirical or mostly depended on experimentations. During the past few decades, many theoretical and computational methods have been developed in strong interaction with experimentalists to design high-performing heterogeneous catalysts. Methods for computational catalyst design can be generally classified into two groups: first-principle and data-driven approaches. The first-principle method studies the reaction mechanism, quantifies the rates of elementary steps, and uses computational techniques to find promising catalysts. In data-driven catalyst design, an empirical structure-performance relationship model is usually built from experimental or computational data. Once established, the model can be used to predict the performance of various catalysts.

2.1 First-principles catalyst design

One of the earliest works on theoretical catalyst design can be attributed to [2], who proposed a systematic catalyst design framework based on reaction mechanism analysis and quantum chemical calculation. The framework is modified and updated herein. As shown in Fig. 2, the computation starts with a proposal of a reaction mechanism, based on which the main reactions, reaction intermediates, and elementary steps are identified. For those reactions that are not well understood, an initial guess of the reaction mechanism has to be postulated based

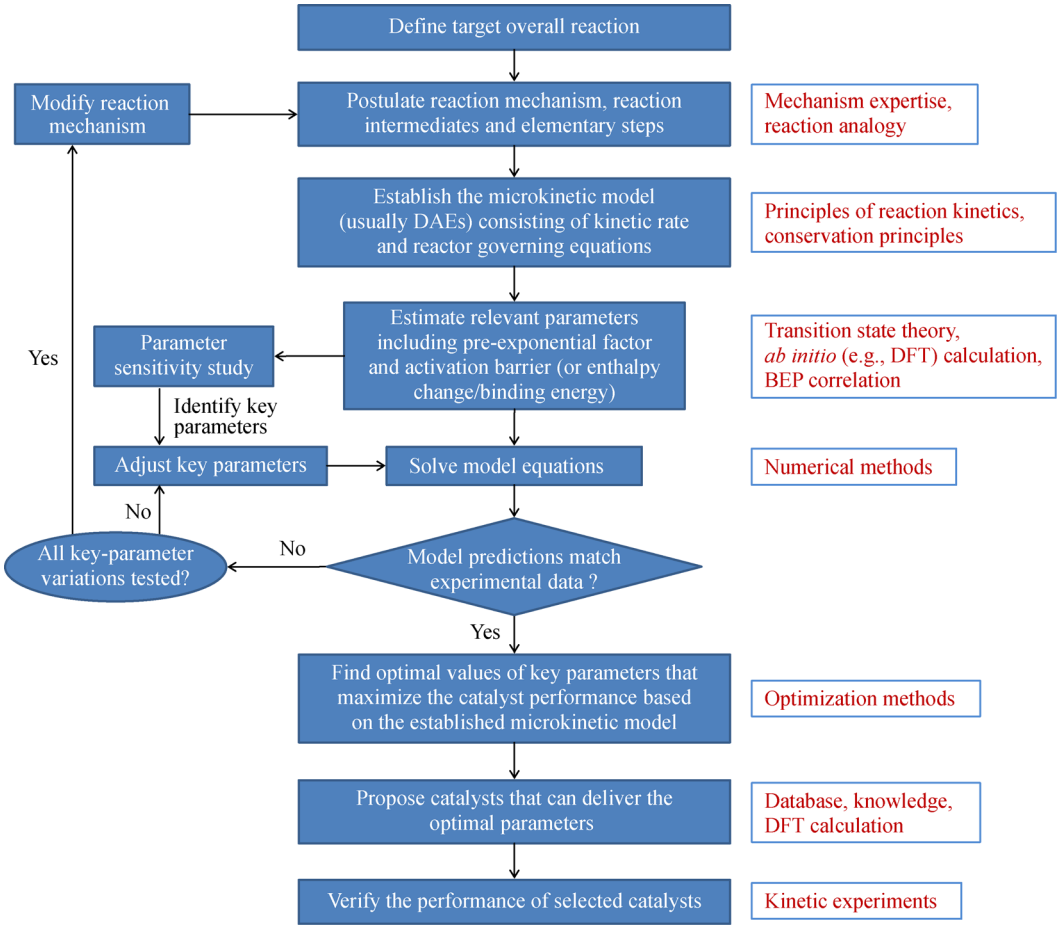

Fig. 2 Catalyst design framework modified and updated from [2].

on the expertise (knowledge) or analogy to other similar reactions.

One of the key steps in catalyst design is to establish a reliable microkinetic model based on the proposed reaction mechanism. Unlike the macrokinetic model, microkinetic models provide fundamental and quantitative insights into the heterogeneous reactions by incorporating knowledge of elementary reactions taking place on the catalyst surface. This characteristic makes it possible to use first-principle (mainly density functional theory, DFT) calculations to predict macroscopic reaction properties such as reaction rate for a given catalyst. The whole microkinetic model is usually expressed by a set of ordinary differential and algebraic equations (DAEs) with one equation indicating a steady-state relation for each reaction intermediate. The next step is to estimate the parameters involved in the DAEs. Transition state theory can be employed to make estimations on the order of magnitude of the pre-exponential factors for the rate constants. The direct computation of activation energies is quite challenging. However, several groups have found that there is a linear correlation between the reaction activation barrier and the enthalpy change of the reaction, known as the Brønsted-Evans-Polanyi (BEP) relation [3]. This provides a feasible way to estimate the reaction activation energy from the binding energies of reaction species on the catalyst surface, which can be obtained directly from DFT calculations. Considering that different parameters can have distinct influences on the reaction kinetics, parameter sensitivity study can be performed to identify the most significant parameters.

Subsequently, the DAE-based kinetic model is solved and model calibration is performed by comparing the model predictions with experimental observations. If the predictions do not agree with experimental data, the key kinetic parameters must be adjusted systematically within reasonable physical ranges. If agreement cannot be achieved by tuning the parameters, the reaction mechanism must be modified and the above steps have to be repeated. After the kinetic model is calibrated, the best catalyst can be identified by solving an optimization problem where the catalyst performance in terms of the reaction rate, conversion, or selectivity is maximized. In fact, two steps are involved here. First, the optimal values of key parameters are determined from the optimization. Next, based on empirical knowledge, existing database, or DFT calculations, the catalyst designer decides how these optimal parameters can be achieved by changing the nature of the existing catalyst or proposing a new one. Once the optimal catalyst is successfully identified, it should be synthesized and the practical performance can be experimentally validated.

According to the above framework, Katare et al. [4] developed a Reaction Modeling Suites (RMS), a rational, automated, and intelligent system, to help establish microkinetic models to be used for catalyst design. Based on the microkinetic model, a genetic algorithm was employed to search for optimal model parameters that correspond to an improved catalyst performance. The reliability of RMS has been demonstrated on a zeolite-catalyzed propane aromatization reaction. Linic et al. [5] developed a microkinetic model for ethylene epoxidation on Ag catalysts. Kinetic parameters for important elementary steps were either derived from DFT or measured in surface science experiments. The proposed model can successfully reproduce macroscopic properties measured in a microreactor. Based on the microkinetic model, a new Cu/Ag alloy catalyst that is more selective than Ag was identified. Considering the possible uncertainty in the microkinetic model, Lee et al. [6] proposed an efficient method to design catalysts where the uncertainties associated with experimental data are represented as exogenous variables with assumed probability distributions. The method has been successfully applied to the ammonia decomposition reaction where the binding energies of nitrogen and hydrogen, as the key model parameters, were optimized to maximize the reaction conversion. The obtained optimal binding energies were subsequently mapped into an actual catalyst. Xu et al. [7] combined DFT calculation with microkinetic modeling to predict the rate and selectivity of steam reforming of methane on different catalysts. A large number of transition metal catalysts have been screened with respect to their steam reforming activities. Other works employing the catalyst design framework shown in Fig. 2 include Herron et al. [8] and Rangarajan et al. [9] where the CO oxidation and methanol synthesis reactions were investigated, respectively.

Wang and Hu [10] simplified the catalyst design framework into three major steps. For a given catalyst and known reaction mechanism, the energy profile of the reaction species can be obtained from DFT calculation. With this energy profile, the microkinetic model is built and parameterized, based on which the overall turnover frequency (TOF), a reaction rate indicator, can be predicted. The authors expressed catalyst structure, energy profile, and the TOF into a structure matrix $\boldsymbol{r}$, an energy vector $\boldsymbol{e}$, and a scalar variable TOF, respectively. The DFT calculation and micro-kinetic prediction were abstracted and represented as functions $g(\boldsymbol{r})$ and $h(\boldsymbol{e})$, respectively, with $\boldsymbol{e} = \mathrm{g}(\boldsymbol{r})$ and $\mathrm{TOF} = h(g(\boldsymbol{r}))$. The optimal catalyst structure denoted by $\boldsymbol{r}_{\mathrm{opt}}$ can be identified by solving an optimization problem where TOF is maximized.

It is worth noting that in reality many catalyst design studies do not follow strictly all the steps in Fig. 2. For instance, instead of performing rigorous parameter sensitivity study, researchers may identify key parameters based on their reaction knowledge or expertise. A large number of studies have found that the plot of reaction activity (e.g., TOF) against the sorption (or binding) energies of key reaction species or elements (atoms) on the catalyst surface always passes through a maximum, looking roughly like a

triangle or a parabola. This kind of plot is called volcano curve, which is very useful for heterogeneous catalyst design. In fact, this phenomenon can be well explained by imposing the BEP relation (also known as the "scaling relation") on the rate-determining step. Jacobsen et al. [11] obtained the volcano-shaped relation between the ammonia synthesis activity and the nitrogen adsorption energy. Based on this observation, a high-performing catalyst was discovered. Later, Jacobsen et al. [12] found that the position of the maximum of the volcano curve is sensitive to the reaction condition, indicating the significance of performing integrated reactor and catalyst design. Nørskov et al. [13] demonstrated that the TOF of the syngas-to-methane reaction is mainly influenced by two parameters, carbon and oxygen binding energies, ΔE^{C} and ΔE^{O}. As illustrated in Fig. 3, Ru and Co lie at the top of the volcano, which agrees well with the experimental findings. Despite their high reaction performances, Ni is still preferred due to its much lower price. However, the Ni_3Fe alloy catalyst (peak of the volcano) was found to be better and cheaper alternative to Ni.

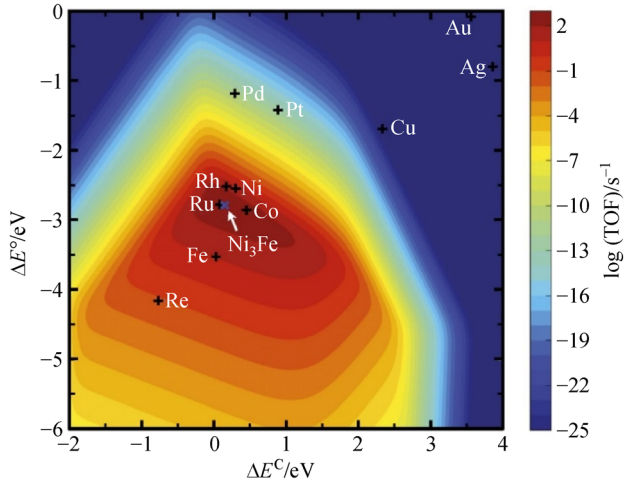

Fig. 3 Two-dimensional volcano contour for the production of methane from syngas, taken from [13]. Reaction conditions are 573 K, 40 bar H_2, and 40 bar CO.

Considering the strong interaction between catalyst selection and reactor operation, Thybaut et al. [14] proposed a systematic method for integrated catalyst and reactor design. The method was exemplified on the oxidative coupling of methane reaction. A reliable microkinetic model was first established and validated from experimental data. Based on this model, the yield of products was then optimized using a genetic algorithm followed by the Rosenbrock and Levenberg-Marquardt method. The decision variables include catalyst descriptors (binding energies of the reaction intermediates), catalyst texture properties (radius of catalyst pellet, porosity, surface area, and tortuosity of catalyst), as well as feed and reactor conditions (feed flow rate and composition, operating temperature and pressure).

2.2 Data-driven catalyst design

Quantum chemical (QC) calculations combined with microkinetic modeling provide the possibility for first-principles catalyst design. However, the large computational cost limits their applications to simple reactions and a limited number of catalyst candidates only. With the rapidly increasing amount of available data as well as the development of catalysis informatics, catalyst structure and activity relationships can now be well described using data-driven machine learning (ML) models. Typically, these models are trained with computational or experimental data and later used for the systematic screening or optimal design of new catalysts to improve the reaction activity.

Huang et al. [15] developed a data-driven catalyst design framework where an artificial neural network (ANN) model is employed to describe the relation between catalyst composition and performance. A hybrid genetic algorithm was proposed and used to find the optimal catalysts based on the ANN model. The design strategy consists of the following steps. (1) An ANN model is first established from an initial set of training data, comprising several catalysts designed by the orthogonal experiment method. (2) Based on the trained ANN model, a few promising catalysts can be identified to maximize the reaction performance by solving an optimization problem using the genetic algorithm. (3) These catalysts are synthesized and tested to obtain their actual reaction performance. (4) Compare the actual performance with the predicted results. If the error is acceptable, jump to step 7; otherwise, go to the next step. (5) Add the designed catalysts and experimental performances into the training set. (6) Re-train the ANN model and repeat steps 2–4. (7) Better catalysts are found. The above-described catalyst design method was applied on the methane oxidative coupling reaction. A few high-performance catalysts were found and the C2 hydrocarbon yield of the best catalyst reached 27.78%, higher than those of the previously reported catalysts.

Baumes et al. [16] successfully employed ANN models to predict catalyst performance for the water gas shift reaction. It was proven that compared to the traditional high-throughput computational and experimental trial-and-error approaches, ML methods possess a great potential in accelerating the discovery of high-performing catalytic materials. Baumes et al. [17] introduced the support vector machine (SVM) model to predict the activities of heterogeneous catalysts for light paraffin isomerization. The advantages of SVM compared to other ML techniques such as ANN were highlighted. Corma et al. [18] illustrated how spectral characterization descriptors can be used for the construction of catalyst performance

prediction models. Principal component analysis was first employed to extract the desired spectral descriptors from the X-ray diffraction characterization of the catalyst. Performance prediction models were then derived using ANN and decision tree methods. Through the application to an epoxidation reaction, it was proven that the use of spectral descriptors can remarkably improve the prediction accuracy of the catalyst reactivity model.

Fernandez et al. [19] developed ANN models to predict the catalytic activities of platinum nanoparticles from their structural characteristics such as particle diameter, surface area, and sphericity. It was demonstrated that the trained ANN model can rapidly estimate the catalytic performance of nanomaterials at a relatively high accuracy. Li et al. [20] developed ML models for fast screening of transition metal catalysts using easily accessible catalyst descriptors as the model inputs. The descriptors include the local electronegativity and effective coordination number of an adsorption site as well as the intrinsic properties of active metal atoms such as the ionic potential and electronic affinity. The trained models were used to screen multimetallic alloys for electrochemical CO_2 reduction. Several promising catalyst candidates were identified.

Goldsmith et al. [21] recently conceptualized a data-driven catalyst development workflow (see Fig. 4) where instead of directly estimating catalyst activities, ML is used to predict the interatomic potentials (potential energy of a system of atoms) trained with data generated from QC calculations. Based on the model predictions, stable catalyst structures under operating conditions are determined. Later, mechanistic analysis and microkinetic simulations can be performed to extract catalyst design insights and make catalytic performance predictions, which can next be verified by catalyst synthesis, characterization, and testing. The potential energy of the synthesized catalysts can be obtained by *ab initio* calculations to close the workflow cycle.

Despite the popularity and high-efficiency of data-driven methods for catalyst development, one needs to be careful when applying these methods. First, a large effort should be invested in the selection of catalyst descriptors. To find a suitable set of catalyst theoretical descriptors is always the prerequisite. Second, unlike the first-principles design method, an accurate ML model prediction is usually limited to the catalysts and reaction conditions similar to those used in model training. In order to increase the robustness of the model and to ensure a highly reliable design result, a substantial amount of representative training data should be used.

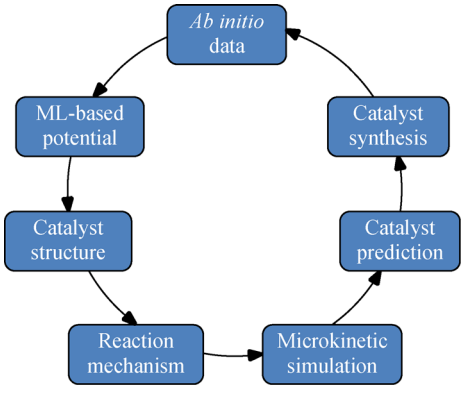

Fig. 4 Machine-learned interatomic potentials for catalyst structure searches [21].

3 Material design for gas separations

Gas separations, such as carbon capture and natural gas sweetening, play significant roles in reducing the environmental impact and cost of industrial processes. Solvent-based absorption and porous material-based adsorption are the most commonly used technologies for separating gas mixtures. In this section, representative works on solvent and porous materials design for gas separation are reviewed.

3.1 Solvent design

Solvents, as important mass separation agents, are widely used in various separation processes. When considering the large number of existing solvents and the necessity for finding new solvents, systematic methods for optimal solvent design are significant [22]. During the past few decades, the computer-aided molecular design (CAMD) method [23] has been widely used for optimal solvent design [24−28]. Considering the strong interactions between solvent selection and process operation, integrated solvent and process design is also essential [29−33]. Figure 5 shows the schematic diagram for solvent and process design using the CAMD method. Starting with solvent molecular structure, solvent properties are predicted via various types of predictive models. Substituting these properties into process models, the performance of solvent-based processes can be predicted. The optimal solvent structure as well as the best process conditions can then be reversely determined by solving an optimization problem where the process performance is maximized. In this section, representative works on CAMD-based solvent

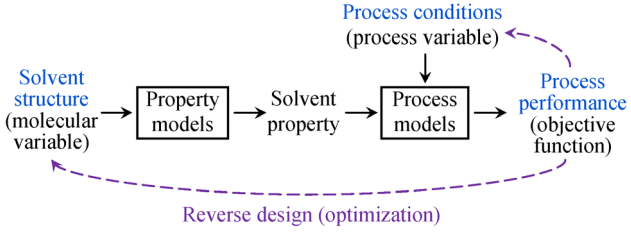

Fig. 5 Schematic diagram for solvent and process design using the CAMD methodology.

design as well as integrated solvent and process design for gas separation applications are reviewed.

Bardow et al. [29] proposed a CAMD method for integrated solvent and process design. Solvent molecules are represented by a set of molecular-specific thermodynamic parameters. These parameters are simultaneously optimized with the process operating conditions. Afterwards, the optimized molecular parameters representing an ideal hypothetical molecule are mapped onto an existing solvent. The method has been successfully used to design solvents for pre-combustion CO_2 capture. Improvements of the separation performance were obtained compared to the reference solvent methanol. Burger et al. [30] proposed a hierarchical decomposition method for integrated solvent and process design. The reliability and efficiency of the method have been demonstrated on a CO_2/CH_4 separation process. The best solvent with optimal process performance was found to be poly(oxymethylene)dimethylether.

Papadopoulos et al. [34] attempted to search for optimal solvents for CO_2 chemisorption. First, a large number of solvents were screened out based on their thermodynamic, kinetic, and sustainability behaviors. Second, high-performing solvents were further screened using a more detailed thermodynamic model to accurately predict the chemical and phase equilibrium of the solvent-water-CO_2 mixtures. As a result, a few promising solvents were successfully identified and assessed. Ahmad et al. [35] used the CAMD method to design chemical solvents for post-combustion CO_2 capture. The work consists of five steps: (1) Problem formulation; (2) generation of solvent candidates using the ProCAMD tool in the ICAS software [36]; (3) prediction of the reaction mechanism between the solvent candidate and CO_2; (4) evaluation of process performance by calculating the heat required for the solvent regeneration; and (5) selection of the best solvent based on the process performance. In total, 25 promising chemical solvents were successfully identified and substantial energy savings for solvent regeneration (up to 31.4%) can be achieved compared to the conventional solvent monoethanolamine.

Recently, ionic liquids (ILs) have attracted much attention as alternatives to conventional organic solvents for separating gas mixtures. Due to the large number of cations and anions making up the ILs, experiment-based IL selection is very tedious and costly. Fortunately, the CAMD method has been successfully extended to IL design. Chong et al. [37] used the CAMD approach to design ILs for carbon capture. The UNIFAC model [38] was used to predict CO_2 solubility in different ILs and group contribution (GC) methods were employed to estimate the thermophysical properties of the ILs. The best ILs were identified by solving an optimization-based computer-aided ionic liquid design (CAILD) problem where the CO_2 absorption capacity was maximized. As a result, 1-decyl-3-methylimidazolium tetrafluoroborate was found to be the best solvent. Considering the strong interactions between solvent selection and process operation, Chong et al. [33] proposed a method to simultaneously design IL solvent and carbon capture process. Disjunctive programming was introduced to find optimal process conditions while the IL design problem was solved via CAMD. Valencia-Marquez et al. [39] performed another IL and process design work for CO_2 capture. IL physical properties were estimated by GC models and the vapor-liquid equilibrium was predicted by an empirical thermodynamic model. The integrated design problem was formulated and solved as a mixed-integer nonlinear programming problem. A multi-objective optimization strategy was employed to handle conflicting design objectives related to process economics and environmental impact.

Peng et al. [40] developed a GC model to quickly estimate IL σ-profiles and V_{COSMO}, two parameters required to perform activity coefficient calculation using the COSMO-SAC (Conductor-like Screening Model — Segment Activity Coefficient) method [41]. With this GC model, an optimization-based CAILD problem was formulated and solved to identify the best ILs for post-combustion CO_2 capture. In order to design ILs for natural gas purification, Mortazavi-Manesh et al. [42] proposed a thermodynamic method to predict the solubility of CO_2, H_2S, CH_4, and C_2H_6 in ILs at 298.15 K and 20 bar. Specifically, the Conductor-like screening model for realistic solvents (COSMO-RS) model [43] was used to predict the activity coefficient of gases in ILs and a cubic equation-of-state was employed to calculate the vapor-phase fugacity coefficient. Over 400 ILs were designed and ranked according to their absorption selectivities of CO_2 and H_2S over CH_4 and C_2H_6. Zhao et al. [44] predicted Henry constants of 12 different gases in more than 10000 ILs at 313.15 K using the COSMO-RS model. Based on the predicted data, a systematic IL screening framework was developed for the optimal selection of ILs to separate specific gas mixtures. Two important gas separation tasks, CO_2/CH_4 and C_2H_2/C_2H_4, were investigated and promising IL solvents were identified for both tasks.

3.2 Porous materials screening

Porous materials are crystalline framework structured materials with pores and cages. Zeolites are the most important porous materials that have shown excellent potential as adsorbents. Recently, metal-organic frameworks (MOFs), emerged as a new type of porous material, have attracted more and more attention for gas separation due to their tunable pore sizes, large surface areas, high porosities, good thermal and mechanical stabilities. Compared to zeolites, the structures of MOFs can be controlled to a much higher degree through variations in the types of the organic linker and the metal. During the past few decades, molecular simulation techniques such as the grand canonical Monte Carlo (GCMC) and molecular

dynamics (MD) simulations have been significantly developed. For gas separation, the GCMC simulation is normally used to predict the equilibrium loading (adsorption isotherm) of gases and MD simulations are used to quantify the diffusion properties of gases in the material. This section briefly summarizes the recent work on computational porous materials design for gas separations.

Hasan et al. [45] proposed a hierarchical computational method combining zeolite screening with separation process optimization. As illustrated in Fig. 6, the computation starts with a three-dimensional pore characterization [46] to obtain a short list of zeolite candidates as potential adsorbents based on shape, size, and pore selectivities. The other filtering is performed based on adsorption selectivity obtained from the isotherms of gases being separated. For the remaining zeolites, the optimization of a pressure-swing adsorption or vacuum-swing adsorption process is carried out and afterwards, a ranked list of zeolites based on the total process cost is finally obtained. The approach was applied to a post-combustion carbon capture process. Later, First et al. [47] applied the above method to select zeolites and adsorption process conditions for CH_4/CO_2 separation. A minimal purity of 97% and recovery of 95% were introduced as hard constraints. Eight novel zeolites were identified for efficiently removing CO_2 from CH_4. The separation cost was minimized through hierarchical material screening combined with rigorous process modeling and optimization. Liu et al. [48] further extended the method to the removal of H_2S from industrial gas mixtures including acid gas (H_2S/CO_2), tail gas (H_2S/N_2), and natural gas (H_2S/CH_4). Several novel and cost-effective zeolites were identified for each purification process.

MOFs are composed of metal nodes and organic linkers. Their functionalities can be well tuned by optimally selecting and/or changing the combination of metals and linkers, which provides them great potential as tunable materials for gas separations. Erucar and Keskin [49] summarized the fundamental steps for large-scale computational screening of MOFs (see Fig. 7). First, a MOF database is constructed and the structural properties such as pore size and surface area are determined [50]. GCMC and MD simulations are then performed to quantify the adsorption and diffusion of gases in MOFs, respectively. Data obtained from molecular simulations are used to calculate separation performance metrics of MOFs. From the performance metrics, MOFs can be finally ranked and the most promising materials are targeted for further experimental validation. The structure-performance relationship analysis is performed either for all the MOFs or only for the promising ones to obtain insights into the design of new structures that can give better separation performance.

Bae and Snurr [51] introduced five adsorbent performance metrics including CO_2 uptake and working capacity, regenerability, and selectivity to assess the potential of over 40 MOFs for CO_2 separation from flue gas, natural gas, and landfill gas. Comparisons with other materials such as zeolites were made and the relations between MOF properties and their separation performances were analyzed. Wu et al. [52] computationally examined 105 MOFs for CO_2/N_2 separation under industrial conditions. A structure-performance relationship

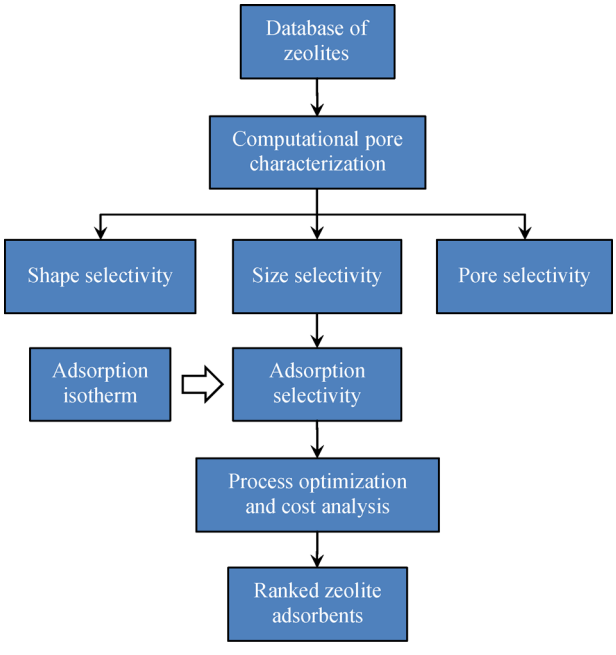

Fig. 6 Hierarchical computational approach for zeolite adsorbent screening, adapted from [45].

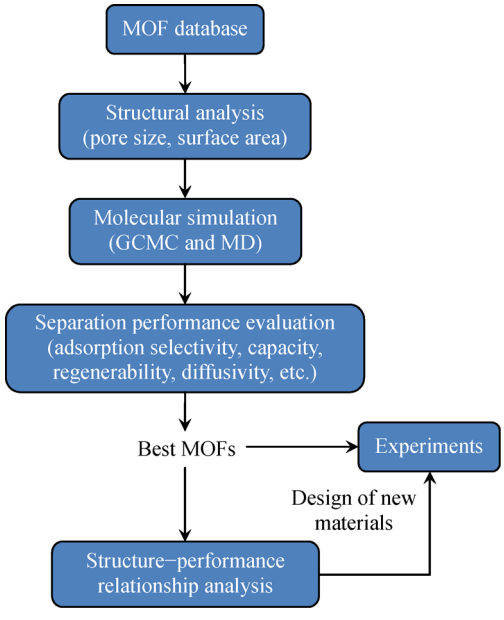

Fig. 7 Method for computational MOF screening, adapted from [49].

model was built to rationalize the resulting CO_2/N_2 selectivity of MOFs. The result shows that the heat of adsorption of pure CO_2 and N_2 as well as the porosity of the adsorbent are the main factors influencing the adsorption selectivity of the MOFs. Later, Wu et al. [53] studied the performance of MOFs to remove CH_4 from H_2. The top MOFs show either higher adsorption selectivity with similar working capacity or higher working capacity with similar selectivity, compared with the traditional adsorbents such as carbonaceous materials and zeolites. Haldoupis et al. [54] computationally screened 500 MOFs to separate CO_2 from N_2. Two MOFs, experimentally known to be stable upon solvent removal, with extremely high CO_2/N_2 adsorption selectivity were identified.

Li et al. [55] investigated the performance of 151 MOFs for CO_2/CH_4 separation via temperature swing adsorption. The energy consumption for material regeneration was adopted as an important performance index. Cu-TDPAT was found to be the best adsorbent showing a minimal energy consumption. Qiao et al. [56] employed molecular simulation to screen 4764 MOFs for removing CO_2 from fiue gas and natural gas. Quantitative relationships were established, for the first time, between the type of metals and the adsorbent performance. It was found that most of the top 30 MOFs contain lanthanides. The same group screened 137953 hypothetical MOFs generated from the libraries of metals and organic linkers for membrane-based natural gas purification [57]. Twenty-four MOFs were prescreened for CO_2/CH_4 and N_2/CH_4 separations. Among them, 5 best MOFs were finally identified for separating the three-component $CO_2/N_2/CH_4$ mixture at 298 K and 10 bar. It should be noted that membrane-based separation is different from the conventional adsorption-based one. In addition to the adsorption performance, diffusion and permeation of the materials need to be taken into account when selecting MOFs for membrane separation. Wilmer et al. [58] built a MOF database consisting of over 130000 hypothetical MOFs. Clear correlations between MOF structural features (e.g., pore size, surface area, functional groups) and their adsorbent performance metrics were obtained. Li et al. [59] screened ~10000 hypothetical MOFs with mixed linkers and functional groups for CO_2 capture using GCMC simulations. The results demonstrate that functionalization enhances carbon capture performance of MOFs when compared to their unfunctionalized counterparts. Considering that computational material screening requires significant computational cost when exploring a large database, Chung et al. [60] developed a genetic algorithm based method to efficiently find top adsorbents for pre-combustion CO_2 capture from a large database of hypothetical MOFs without simulating all the candidates one by one. The identified high-performing MOFs were synthesized and evaluated. They showed a high CO_2 working capacity as well as a high CO_2/H_2 selectivity. One of the synthesized MOFs even showed a CO_2 working capacity higher than any MOF reported in the previous literature.

The group of Keskin has contributed much work in large-scale computational MOF screening. Gurdal and Keskin [61] used GCMC and MD simulations to study the performance of 10 common MOFs for noble gas Xe/Kr and Xe/Ar separations. It was found that MOFs were promising materials for Xe/Kr and Xe/Ar separations due to their high Xe selectivity and permeability. Erucar and Keskin [62] employed the same method to assess the potential of 10 bio-MOFs for natural gas purification. The bio-MOFs are composed of biocompatible metal cations and linker molecules such as amino acids and sugars. Results show that several bio-MOFs outperform the widely studied MOFs and zeolites in both adsorption-based and membrane-based CO_2/CH_4 separations. Using the same method, Altintas and Keskin [63] screened 278 different MOFs for the separation of C_2H_6/C_2H_4 and C_2H_6/CH_4 mixtures. Later, Sumer and Keskin [64] computationally examined the performance of 100 MOFs for the separation of CO_2/CH_4, CO_2/N_2, and CO_2/H_2 mixtures under different operating conditions. The results demonstrate that regenerability is a very important performance metric for screening materials in the first step and later MOFs can be ranked according to their adsorption selectivities. The relationships between structural properties of MOFs and the separation performance were examined. It was found that materials with pore sizes of 4–7 Å, surface areas of 200–800 m^2/g, and porosities of 0.18–0.50 were the best adsorbents. Azar and Keskin [65] performed a molecular simulation study to investigate the performance of 174 different MOFs for separating C_2H_2/CO_2 and C_2H_2/CH_4 mixtures. Based on the evaluation of several different adsorbent performance metrics, the best MOFs were identified for both separations. The structure-performance relationship was analyzed to guide the experimental synthesis of new powerful MOFs.

4 Conclusions

Functional materials with tailored properties often represent the heart of process industry advances. Compared to the experimental trial-and-error method, computational approaches show large advantages in searching for existing high-performance materials and exploring new powerful candidates. A chemical process usually employs several different types of materials. This article chooses to focus on two most important process materials, namely heterogeneous catalyst and gas separation agent. Theoretical methods and recent representative works on computational design and screening of these two materials are reviewed. Due to the constantly improving theoretical modeling tools as well as the rapid growth of computer power, the significance of computational methods for functional

materials research and development will continue to increase.

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